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Nonlinear Rheology of Unentangled Polymer Melts Reinforced with High Concentration of Rigid Nanoparticles

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Abstract A scaling model is presented to analyze the nonlinear rheology of unentangled polymer melts filled with high concentration of small spherical particles. Assuming the majority of chains to be reversibly adsorbed to the surface of the particles, we show that the emergence of nonlinearity in the viscoelastic response of the composite system subjected to a 2D shear flow results from stretching of the adsorbed chains and increasing desorption rate of the adsorbed segments due to the imposed deformation. The steady-state shear viscosity of the mixture in nonlinear shear thinning regime follows the power law $\eta \sim \dot{\gamma}^{-1/2}$, where $\dot{\gamma}$ is the applied shear rate. At large strain amplitude γ_0 , the storage and loss moduli in strain sweep tests scale as $G' \sim \gamma_0^{-1}$ and $G'' \sim \gamma_0^{-1/2}$, respectively.

Keywords Rheology · Polymer nanocomposites · Melt · Scaling relations · Nonlinearity

Introduction

Stable dispersion of sub-micron solid particles in polymer melts and solutions can be achieved in the presence of favorable polymer–particle interactions. Studying the rheological behavior of polymer composites reinforced with well-dispersed nanoparticles, often referred to as polymer nanocomposites (PNCs), has been the subject of a growing number of experimental and theoretical studies in the past decade [1–10]. A notable observation is the qualitative resemblance between the thermomechanical response of

PNCs and that of polymer thin films confined between planar surfaces [11–13]. This similarity implies that the adsorption of polymer chains on the surface of nanoparticles alters the mobility of the chains far into the bulk, and therefore the mixture cannot be simply envisioned as a dispersion of hard particles interacting in a matrix.

PNCs generally exhibit strong nonlinear viscoelastic behavior in the response to dynamic inputs. Typical examples of such nonlinear characteristics are strong shear thinning at relatively low shear rates or strain-dependent viscoelastic moduli at low strain amplitudes (Payne effect). In the present Letter, we use a scaling model to elucidate the nonlinear rheological features of the nanofilled unentangled polymer melts by considering the effect of energetic affinities between polymer and particles. The model is particularly relevant to PNCs with high filler concentration where the majority of polymer chains in matrix can interact energetically with the adhesive surface of dispersed particles. Structural and flow properties of colloidal suspensions of this kind have been the subject of recent experimental studies of Anderson and Zukoski [14, 15].

Scaling Analysis

Consider a suspension of non-aggregated rigid spherical particles in an unentangled polymer matrix. Each chain in polymer melt is comprised from N statistical segments with length a and excluded volume v , such that at equilibrium the chain's radius of gyration is $R_g \sim aN^{1/2}$. The energetic affinity E_{ad} between the polymer segments and the surface of particles is short range and weak, on the order of the thermal energy $k_B T$ (henceforth, $k_B T$ is taken to be the unit of energy). As a result, polymer chains reversibly bind to the solid surface and build a layer around particles which

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can be described as a continuous succession of loops and tails at different sizes (Fig. 1a). At equilibrium, the reversible adsorption of flexible chains onto an adhesive solid surface leads to a fluffy layer with a self-similar structure [16]. The description of the curvature effects on the self-similar structure of the adsorbed layer was initially proposed by Aubouy and Raphaël [17]. These authors reported that when the characteristic size of the polymer, R_g , is much smaller than the particle size R , the extent of the self-similar structure is limited by polymer dimensions alone. In other words, the colloid curvature is not relevant, and the polymer can be considered as if adsorbed on a flat surface. In the real experimental cases, the condition $R \gg R_g$ is granted considering the size of flexible polymer chains in unentangled regime (a few nanometer) compared with the smallest size of commercially available nanoparticles (tens of nanometer). Henceforth, this condition is assumed to be valid in this paper.

Let us assume that the composite system undergoes a plane Couette flow with shear rate of $\dot{\gamma}$, where the velocity field follows $u_x = \dot{\gamma}y$ and $u_y = u_z = 0$. The polymer matrix is comprised from a population of two types of chains: chains

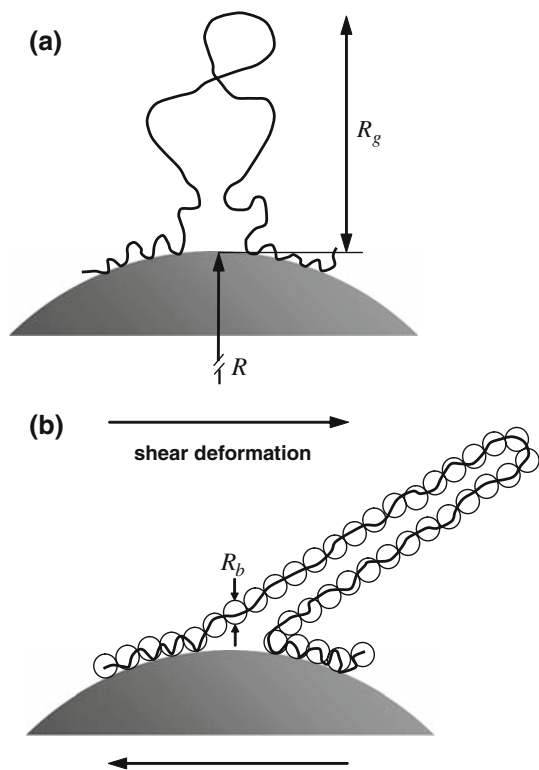


Fig. 1 **a** Schematic of the equilibrium configuration of a Gaussian flexible chain with size R_g in a polymer melt, adsorbed on a spherical particle with radius $R \gg R_g$. The adsorbed chain consists of loops, tails and sequences of bonded segments. **b** At sufficiently large shear deformation (rate), the adsorbed polymer chain stretches in the direction of the flow. The stretched chain can be pictured as a close-packing of subunits called blobs, each of size R_b , within which the structure of the chain is still Gaussian

that are adsorbed to the surface of the particles, and chains that are not adsorbed (at least on the time scale of $\dot{\gamma}^{-1}$). The average shear stress produced in the polymer matrix can be approximated as $\sigma_{xy}^m = f\sigma_{xy}^a + (1-f)\sigma_{xy}^f$, where f is the fraction of adsorbed chains, and σ_{xy}^a and σ_{xy}^f are the average shear stress produced by adsorbed and free chains, respectively.

The average friction acting on a free segment in the bulk reads $\xi_0 \sim \tau_0/a^2$, where τ_0 represents the average relaxation time of a free segment in the bulk. Due to the adhesion, the adsorbed segments undergo a larger friction ξ_1 and maintain a longer residence time τ_1 on the adhesive colloidal surface. In equilibrium, the relation between τ_1 and τ_0 is given by $\tau_1 = \tau_0 \exp(E_{ad})$. The principal Rouse relaxation time of the adsorbed chains, $\tau_a \sim R_g^2 \xi_a$, is also expected to be larger than that of the free chains, $\tau_f \sim R_g^2 \xi_f$, where ξ_a and ξ_f indicate the friction on the adsorbed and free chains, respectively.

When the shear deformation rate $\dot{\gamma}$ exceeds τ_a^{-1} , the adsorbed chains are expected to be tilted and stretched by the shear flow (Fig. 1 b). Each stretched chain can be pictured as a string of N_c Pincus blobs of size R_b [18]. Inside each blob, the chain statistics is still Gaussian, i.e., for a blob containing N_b segments ($N_b = N/N_c$), $R_b \sim a N_b^{1/2}$ with Rouse time of $\tau_b \sim R_b^2 \xi_b$, where ξ_b is the friction acting on each blob. Since the polymer segment within each blob remains relaxed, the tension on each blob exerted by neighboring blobs can be determined by the condition $\dot{\gamma} \tau_b \sim 1$. This way, the friction experienced by each blob forming the dragged polymer is $\xi_b \sim R_b^{-2} \dot{\gamma}^{-1}$. Since $R_b \dot{\gamma}$ represents the velocity difference between the top and bottom of each blob, the force in the blob is $F_b \sim \xi_b R_b \dot{\gamma}$ or $F_b \sim R_b^{-1}$. Accordingly, the shear rate-dependent size of the blob reads $R_b \sim (\xi_b \dot{\gamma})^{-1/2}$, implying that the blob size shrinks as the applied shear rate on the system increases.

In strong shear regimes, when $\dot{\gamma} > Na/R_g \tau_a$, adsorbed chains elongate to their maximum length ($\sim Na$) and the size of adsorbed blobs becomes comparable with a . The time required for this elongation is on the order of $\tau \sim Na/R_g \dot{\gamma}$. At this stage, the entropic force developed within each blob of dragging chains reaches $F_b > a^{-1}$, during a time scale much smaller than the chain's Rouse time. As a result, the residence time of the adsorbed blobs reduces to $\tau_1 = \tau_0 \exp(E_{ad} - F_b \lambda)$, where λ is an activation length (similarly, we have $\xi_1 = \xi_0 \exp(E_{ad} - F_b \lambda)$). For the weak and short range polymer–particle energetic interactions considered here, we have $E_{ad} \sim 1$ and $\lambda \sim a$. Hence, at strong shear rates of $\dot{\gamma} > Na/R_g \tau_a$, the imposed shear rate regulates the unzipping of adsorbed segments from the adhesive particles. During such shear mediated desorption, the blob force F_b is counterbalanced by the friction force acting on the unzipping segments. Hence, the

shear stress developed inside the layer of adsorbed blobs is $\sigma_{xy}^a \sim cR_b\xi_b\dot{\gamma} \sim c(\xi_b\dot{\gamma})^{1/2}$, where c is the steady-state surface density of blobs attached on the particle at a given shear rate. The mean number of the adsorbed blobs (per unit colloidal surface area) is given by $c = c_{eq}\tau^*/\tau$, where τ^* is the average desorption time of a blob and $c_{eq} \sim a/v$ (i.e., colloidal surface is assumed to be saturated at equilibrium). Assuming $\lambda \sim a$, the desorption time τ^* can be estimated as $\tau^* \sim \lambda/(a\dot{\gamma}) \sim \dot{\gamma}^{-1}$ which leads to $\sigma_{xy}^a \sim \dot{\gamma}^{1/2}$. The contribution of strongly stretched free chains in stress production can be estimated using the virial equation $\sigma_{xy}^f = \frac{1}{Nv} \sum_{n=1}^N \langle F_b^{(n)} R_b^{(n)} \rangle \sim N\xi_0 a^2 \dot{\gamma}/v$, where index n refers to the n th blob along the highly stretched free chain, and $\langle \dots \rangle$ indicates ensemble averaging. Note that for highly filled systems with small particles, $f \sim 1$ and the contribution of free chains in stress production is negligible.

The overall shear stress developed in the composite, σ_{xy} , can be calculated from the bulk stress using $\sigma_{xy} = h\sigma_{xy}^m$, where function h accounts for hydrodynamic interaction between pairs of the rigid particles. For an incompressible polymer melt, filled with rigid particles, h is a function of the volume fraction Φ and geometry of the particles [19]. This way, we have $\sigma_{xy} \sim h(\Phi)c(\xi_b\dot{\gamma})^{1/2}$, and therefore the overall viscosity scales as $\eta \sim \dot{\gamma}^{-1/2}$. This conclusion is compared with the recent experimental results by Anderson and Zukoski [14]. Figure 2 shows the steady-state relative viscosity of unentangled polyethylene oxide (PEO) melt with molecular weight of 400 and 1,000, reinforced with 48

vol% and 45 vol% of spherical silica nanoparticles (with average diameter of 43 nm), respectively. The line with slope $-1/2$ shows the slope of shear thinning predicted by our scaling analysis which is in reasonable agreement with the slope of the experimental data.

The scaling theory described here can also be used to rationalize the strain-dependent storage and loss moduli of PNCs, a phenomenon which is often referred to as Payne effect. Reduction of the viscoelastic moduli at large amplitude oscillatory flows ensues essentially for the same reason as discussed above: at large amplitudes, stretching chains along the direction of the flow enhances the desorption of the segments from the particle surface, thereby contributing in dissipation of the applied energy. Consider an oscillatory strain $\gamma = \gamma_0 \sin(\omega t)$ with frequency ω and strain amplitude γ_0 imposed on the composite with $f \sim 1$. At low frequencies ($\omega < \tau_a^{-1}$), the loss modulus follows $G'' \sim \omega\eta$ [20] where viscosity scales as $\eta \sim (\gamma_0\omega)^{-1/2}$ as demonstrated above. Therefore, at large amplitude $\gamma_0 > Na/(R_g\omega\tau_a)$ and concurrent with deformation-mediated desorption of the blobs, we have $G'' \sim \gamma_0^{-1/2}$. If $\delta(\omega)$ shows the phase angle between stress and strain, the storage and loss moduli of the system can be connected to each other using $\tan \delta = G''/G'$, where at low frequencies $\tan \delta = G''/G' \sim (\omega\tau_a^s)^{-1}$. The time scale τ_a^s represents the relaxation time of the stretched adsorbed chains; that is the time required for an adsorbed stretched chain to diffuse a distance comparable with Na [21]. The speed of diffusion along the length of stretched chain is $R_b\omega\gamma_0$ with $R_b \sim (\xi_b\omega\gamma_0)^{-1/2}$. This way $\tau_a^s \sim Na/(R_b\omega\gamma_0) \sim Na(\xi_b/\omega\gamma_0)^{1/2}$ and consequently the storage modulus at large amplitudes scales as $G' \sim \gamma_0^{-1}$. These findings are comparable with experimental observations of Anderson and Zukoski [15] where the storage and loss moduli of highly filled PEO (molecular weight of 400) are measured to decrease with strain amplitude as $G' \sim \gamma_0^{-1.1}$ and $G'' \sim \gamma_0^{-0.6}$, respectively.

Conclusion

In summary, the presented analysis shows that owing to the reversible adsorption of the polymer chains onto the solid surface of adhesive particles (and therefore deceleration of chain relaxation), applied energy by external deformations during a fast flow can be stored in the stretched polymer chains, instead of being dissipated by their chain-scale Rouse-like relaxation. The nonlinear response of the system is mediated by unbinding the elongated polymer chains from the particles. As the relaxation process is suppressed in adsorbed chains, the nonlinearity is expected to emerge at smaller strain rates and amplitudes compared with the onset of nonlinearity in the neat polymer. The overall

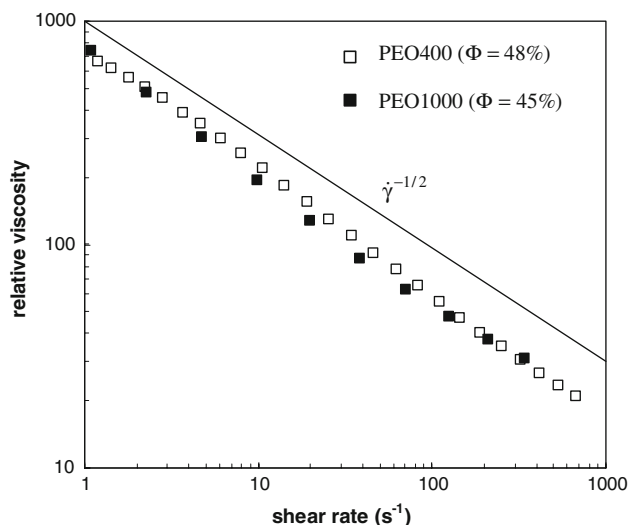


Fig. 2 Steady-state shear viscosity of PEO-silica composites (normalized by the zero shear rate viscosity of neat PEO) as a function of shear rate [14]. PEO melts are reinforced with spherical silica particles with $R = 43$ nm (open squares: PEO melt with molecular weight of 400 filled with 48 vol% silica particles; filled squares: PEO melt with molecular weight of 1,000 filled with 45 vol% silica particles). Solid line shows $\dot{\gamma}^{-1/2}$

viscoelastic properties of the system in nonlinear regimes exhibit a universal dependence on the applied deformation (rate) in highly filled systems, where majority of the polymer chains are in contact with the surface of the particles. The resulting scaling relations are expected to be valid for the systems with spherical particles or non-spherical particles having low aspect ratio in geometry.

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